Evaluating the S-isotope fractionation associated with Phanerozoic pyrite burial

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During the Phanerozoic, the sulfur isotopic composition of oceanic sulfate has fluctuated on a timescale of millions of years. This variation is generally thought to be a combination of changes in sulfur fluxes into and out of the ocean and possibly also variations in the isotopic fractionation between seawater sulfate and coeval burial pyrite ($\delta^{34}S_{PY}$). The magnitude of $\delta^{34}S_{PY}$ is principally controlled by microbial sulfate reduction and sulfur disproportionation as well as processes associated with early diagenesis. The magnitude of the $\delta^{34}S_{PY}$ is also useful for constraining sulfur cycle models and for exploring the cause of changes in the sulfur cycle with time.

We have examined constraints that exist for $\delta^{34}S_{PY}$ and the exponent λ that relates variations of the $^{34}S/^{32}S$ to variations of the $^{33}S/^{32}S$, using the multiple sulfur isotope record of seawater sulfate proxies (a subset of the Kampschulte and Strauss (2004) sample set and a compilation of literature data of oceanic sulfate and contemporaneous sulfide). We have evaluated the sulfur isotope record in two ways: one uses the $^{34}S/^{32}S$ of average sedimentary pyrite from a literature compilation, and the other draws on the $^{33}S/^{32}S$ signal of seawater sulfate and sulfur cycle models to provide a constraint that is independent of the record provided by average sedimentary pyrite.

Our data analysis indicates that $\delta^{34}S_{PY}$ and the exponent λ changed during the Phanerozoic from slightly lower values of $\delta^{34}S_{PY}$ (lower values of λ) in the early Phanerozoic (Cambrian–Permian) to higher values of $\delta^{34}S_{PY}$ (higher values of λ) starting in the Triassic. We interpret this change to reflect a change in the proportion of sulfide that was reoxidized and processed by disproportionation processes on a global scale and discuss the implications of this change for the Phanerozoic evolution of the sulfur cycle.

[1] Kampschulte & Strauss (2004) *Chem.Geol.* **204**, 255-286.

Phase stability and elasticity of ScAlO$_3$ at high pressure

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Till now, many $A^{2+}B^{4+}O_3$-type perovskites (pv) have been confirmed to become the post-perovskite (ppv) with the CaIrO$_3$ structure (*Cmcm*) at extreme conditions, such as MgSiO$_3$, CaTiO$_3$, MgGeO$_3$. Here we investigated the high-pressure phase stability and elasticity of perovskite-structured Sc^{3+}Al^{3+}O$_3$ using *ab initio* calculations based on the density function theory, implemented in VASP code.

Three candidate phases of ScAlO$_3$ were considered, *Pbnm*, *Cmcm* and *I*4/*mcm* respectively. A phase transition is observed at 53 GPa and 0 K from *Pbnm* to *Cmcm* according to their enthalpy. For ScAlO$_3$, the *I*4/*mcm* phase is unstable in present pressure range up to 130 GPa although it is a stable high-pressure phase in YAlO$_3$ case [1].

In both *Pbnm* and *Cmcm* phases, nine independent elastic constants show monotonic increases with pressure, and the longitudinal (C_{11}, C_{22}, C_{33}) elastic constants are larger than the off-diagonal (C_{12}, C_{13}, C_{13}) and shear (C_{44}, C_{55}, C_{66}) constants. The post-perovskite elasticity shows significant anisotropy.

A comparison of the compressional wave speed (Vp) and the shear wave speed (Vs) of ScAlO$_3$ with those of MgSiO$_3$ and CaSiO$_3$ [2] and PREM [3] suggests that ScAlO$_3$ is a good analogue to explore the structures and the properties of lower mantle minerals.
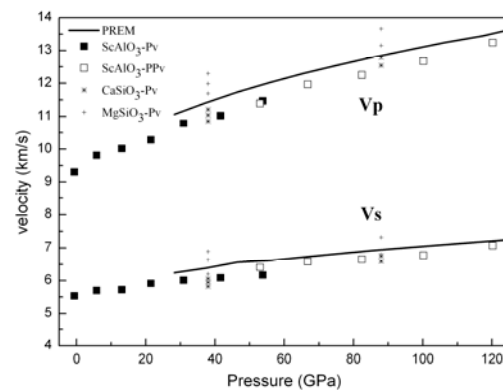

Figure 1: Pressure dependence of the elastic wave speed for ScAlO$_3$.pv and ppv, MgSiO$_3$ and CaSiO$_3$ pv in comparison to PREM.

[1] Wu *et al.* (2006) *J. Phys.: Condens. Matter* **18**, 3907-3916.
[2] Li L *et al.* (2006) *Phys. Earth Planet. Inter.* **155**, 249-259.
[3] Dziewonski *et al.* (1981) *Phys. Earth Planet. Inter.* **25**, 297-356.